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PROCESSING OF ADVANCED CERAMICS WHICH HAVE POTENTIAL FOR USE IN GAS TURBINE AERO ENGINES

by
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MISE EN OEUVRE DE CÉRAMIQUES DE POINTE À USAGE POTENTIEL POUR COMPOSANTS DE MOTEURS D'AVION

by/par

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ABSTRACT

Si_3N_4 and SiC based advanced ceramics that have been produced by hot isostatic pressing (HIP'ing) have good potential to be used as hot section components in gas turbine aero engines. This report provides background for an NAE-SML investigation of this potential. The report begins with a general overview of the many fabrication methods that have been used to produce both monolithic ceramics and SiC whisker reinforced composite ceramics. This is followed by a comprehensive survey of past efforts to produce Si_3N_4 and SiC based ceramics by HIP'ing. It is apparent that many of these efforts have involved HIP'ing of material that has already been densified by sintering, but such an approach does not really allow the full benefits of HIP processing to be realized. On the other hand, HIP'ing of Si_3N_4 based composite produced by reaction bonding may result in ceramic material of superior quality. It also appears that many previous efforts have resorted to incorporating densifying aids into the starting material, even though high temperature properties may suffer as a result. It is suggested that HIP'ing of vacuum encapsulated Si_3N_4 or SiC particulate which contains SiC whiskers for reinforcement, but which does not contain densifying aids, may be a method of producing ceramic material of sufficient quality to be considered for use in gas turbine engines.

RÉSUMÉ

Les céramiques de pointe à base de nitrure ou carbure de silicium, Si_3N_4 et SiC, produites par pressage isostatique à chaud sont des matériaux qui pourraient être utilisés pour certains composants de turbines à gas aéropropulsives. On situe dans ce rapport une étude que se propose d'entreprendre une équipe de l'Établissement national d'aéronautique sur cette utilisation possible. On y résume pour commencer les méthodes de mise en oeuvre utilisées dans la production de céramiques monolithiques et de leurs composites renforcés par whiskers de SiC. On y présente ensuite un examen critique des travaux déjà accomplis sur l'utilisation du pressage isostatique à chaud comme technique de densification. Il ressort de cet examen que dans la plupart des cas, ce sont des matériaux préalablement frittés que l'on a soumis au pressage isostatique à chaud, une approche qui ne permet pas de retirer tous les avantages qu'offre cette méthode de densification. Cependant, il apparaît qu'en soumettant au pressage isostatique à chaud du nitrure de silicium produit par liaison par réaction, on obtienne un matériau de qualité supérieure. Il ressort aussi de cet examen que dans la plupart des cas on a eu recours à des agents de densification, bien que cela ait pu avoir des effets néfastes sur les propriétés du matériau à hautes températures. Finalement, on suggère, d'une part, que le pressage isostatique à chaud d'un mélange de particules de Si_3N_4 ou de SiC et de whiskers de SiC comme renforcissement, encapsulé sous vide sans agent de densification, puisse être une méthode attrayante de fabrication de matériaux composites à base de céramiques, et d'autre part, que la qualité des matériaux ainsi produits puisse être suffisante pour que l'on envisage leur utilisation dans les moteurs d'avion.

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1. Introduction

The term 'ceramic' applies to a diverse class of materials, but can be defined in broad terms as an inorganic, non-metallic material processed or consolidated at high temperature. Materials such as porcelain, refractories, and glass have been in use for generations, and can be thought of as 'traditional' ceramics. In recent years, by careful control over composition and processing, ceramic materials have been developed which exhibit superior thermal, chemical, mechanical, electrical or optical properties. These are so-called 'advanced' ceramics, and include the nitrides, carbides, and oxides of a large number of elements.

Many advanced ceramics have properties which, at first sight, make them attractive for use in demanding structural applications. Table 1 lists mechanical and physical properties of some ceramics and compares them with those of a typical nickel based superalloy. It is apparent that ceramics based on silicon nitride (Si_3N_4) and on silicon carbide (SiC) offer very high stiffness, low densities, and can withstand very high temperatures. This makes them strong candidates to replace nickel and cobalt based alloys in gas turbine aero engine applications, where the ever-present incentive is to run at higher temperatures and pressures in order to improve performance and efficiency. The latest engines now rely on metals technology proven some 20 years ago, and it is widely felt that although continuing development of the existing technology still offers some performance increases, the next leap ahead in engine technology will require completely new materials (see Jeal[1], Drewer[2]). With the potential to retain their properties to 1400°C or higher, ceramics based on Si_3N_4 or SiC are thought to offer the greatest potential to fill this requirement. Note that while Si_3N_4 exhibits somewhat higher strength than SiC, the potential maximum use temperature of Si_3N_4 is somewhat lower than SiC due to the lower decomposition temperature of Si_3N_4.

Other advanced ceramics, including alumina and partially stabilized zirconia, have potential to be used in some high temperature applications, but are not considered to be leading candidates for use in structural components in gas turbine aero engines. Alumina, for example, maintains good corrosion resistance, good stiffness, and good strength at high temperatures, but exhibits very poor thermal shock resistance; an important property to be considered in the steep temperature gradients and with the rapid

temperature fluctuations that are developed in gas turbine engines (see Bennett[3]). Partially stabilized zirconia also suffers from poor thermal shock resistance as well as being a comparatively high density ceramic, and its good strength and toughness properties are maintained only to about 800°C. Zirconia ceramics appear to offer more promise in land based piston engines (see Leach[4]).

There are a wide variety of processes available to fabricate advanced ceramic materials, but the usual way involves first forming particulate raw material (about 1 μm in size) into a 'green' compact, and then 'sintering' at elevated temperature to achieve the solid ceramic. Conventional forming methods include: slip-casting, uniaxial cold pressing, cold isostatic pressing, injection molding, and extrusion molding (see Fig. 1). Some fabrication processes, including uniaxial hot pressing and hot isostatic pressing (HIP'ing), enhance sintering through the application of pressure. Other fabrication processes, such as reaction bonding, are based on in-situ chemical reactions.

These various fabrication methods produce ceramics that are used in a large number of applications requiring resistance to heat and to chemical attack. However, their use in critical structural applications, such as in gas turbine engines, has been precluded by one dominant feature of ceramic materials, namely, their brittleness. The same strong interatomic bonding which gives rise to exceptional heat and chemical resistance also imposes a limited ability to deform plastically and thereby relieve stress concentrations. Consequently, ceramics are particularly sensitive to minute imperfections in their microstructure that serve as nucleation sites for cracking.

In order to improve this situation, much research effort is being directed towards developing fabrication methods that minimize or eliminate microstructural flaws. One technique which shows good promise is hot isostatic pressing (HIP'ing) to consolidate fine-scale ceramic particulates. At present, HIP'ing is successfully used on a commercial basis to produce powder metallurgy parts with no residual porosity, and to heal casting defects.

Also being developed to improve the fracture resistance of ceramics is the idea of incorporating a reinforcing medium into the microstructure to produce a composite material. Provided that the reinforcing particles are of an appropriate size and are suitably distributed, they serve as impediments to crack propagation, and the fracture

resistance of composite ceramic can be much higher than monolithic ceramic. This has been found to be so effective in some uniaxially reinforced ceramic composites that catastrophic brittle failure does not occur, and instead the composite fails by gradual accumulation of damage (see Cornie et al.[5]). Among the more promising reinforcements are microscopic 'whiskers' of SiC measuring about 0.5 μm in diameter and about 10-50 μm long.

Aside from NAE's general interest in advancements in aero engine technology, ceramic composites produced by HIP'ing are of particular interest because of the availability of a HIP facility in the SML. It might be anticipated that the combination of Si_3N_4 or SiC ceramics which incorporate SiC whisker reinforcement, and which are consolidated by a HIP'ing route, can be produced to a sufficiently high quality to be considered for use as structural components in gas turbine engines. This paper provides background for an SML program to investigate HIP processing of Si_3N_4 and SiC based ceramics. It begins with an overview of fabrication methods which have been used to produce both monolithic ceramic and SiC whisker reinforced composite ceramic based on either Si_3N_4 or SiC. This is followed by a comprehensive survey of past efforts to produce Si_3N_4 ceramic and SiC ceramic by HIP'ing. In the final section, the findings are discussed and suggestions for future work are made.

2. Fabrication of Si_3N_4 and SiC Ceramic

As mentioned in the previous section, there are several processes available to fabricate advanced ceramic material. Unlike with metals and plastics, however, the strong covalent bonding typical of many ceramics results in decomposition rather than melting, a behaviour which precludes following a traditional melt-cast-harden route, or a melt infiltration route, to produce material. The usual way to fabricate ceramic components involves first forming particulate ceramic into a green compact, and then sintering at elevated temperature to produce a solid product. Several forming methods are shown schematically in Fig. 1. Often, organic binders and/or plasticizers are used in the forming stage which are then burned out prior to sintering. Reed[6] provides a more detailed treatment of conventional ceramic processing and discusses the use of forming additives. The various forming methods are introduced in Section 2.1, while aspects of sintering which pertain to Si_3N_4 and SiC are reviewed in Section 2.2.

Si_3N_4 and SiC components can also be fabricated via processes, including HIP'ing, which enhance sintering through the application of pressure. These processes are introduced in Section 2.3. Section 2.4 deals with fabrication processes which are based on in-situ chemical reactions. The drawbacks and benefits of the various methods are discussed in Section 2.5.

2.1 Forming

Slip casting is a forming method that has been used since ancient times. The 'slip' (i.e. slurry) - which is made up of ceramic particulate, water, and other lubricants - is poured into a porous mold, and water is drawn from the contact area into the mold leaving a green body. The green body is extracted from the mold, allowed to dry, and is then ready to sinter.

With cold pressing, ceramic particulate is mixed with organic binder (e.g. polyvinyl alcohol), filled into a die, and pressed uniaxially into a green body whose density can be quite close to the final sintered density. For this reason the method can be used to form components requiring close dimensional tolerances, but it is restricted to forming relatively simple shapes.

Cold isostatic pressing overcomes this shape limitation. The ceramic/binder mix is encased in a rubber sheath, the sheath placed in a liquid chamber, and pressure is applied to the liquid. Hydrostatic pressure is transmitted uniformly to the contents of the sheath, and compacts of fairly intricate shapes can be produced.

Injection molding involves mixing ceramic particulate with a relatively large quantity of plastic binder (15-20%), heating the mix, and pressing into a mold. Typically, the binder material is a mixture of polyethylene, paraffin, and petroleum oil. The technique itself is widely used in forming of plastics, and complex shapes can be achieved. When applied to ceramics, however, there are problems associated with a large amount of shrinkage of the compact during burnout of the binder.

Extrusion molding is a forming process which also incorporates a plastic binder, but in this case the ceramic/binder mix is forced through a die orifice to produce compacts having an axis normal to a fixed cross section.

Green bodies of ceramic material can also be formed via chemical synthesis routes such as sol-gel processing and pyrolysis of polymer precursors (see Cornie et al.[5]). Sol-gel processing involves starting with a colloidal solution containing large metal oxide molecules (i.e. the sol) and then polymerizing the molecules into a continuous network (i.e. the gel). The gel is dried, and then sintered. The method appears to be limited to producing green oxide ceramic, although sol-gel processing has been used to produce AlN and Si_3N_4 powders. Polymer pyrolysis can be used to form covalent ceramics, including SiC and Si_3N_4, and involves polymerization of organic starting material followed by heat treatment to decompose the organic polymer to inorganic SiC or Si_3N_4. As with injection molding of ceramics, sol-gel processing and polymer pyrolysis suffer from shrinkage problems.

2.2 Sintering

Once the green body has been prepared, it is ready to be sintered. The term sintering covers the processes by which the original particulates join together to form a solid mass. This consolidation is often accompanied by a reduction in the free spaces between particles and in the overall volume. General aspects of sintering are discussed by Davidge[7] and by Mitchell and Hendry[8], and a summary is presented below. More detailed aspects of sintering Si_3N_4 and SiC are presented by Greskovich and Prochazka[9], and by Ziegler et al[10].

In its simplest form, sintering involves heating the green compact, typically to about 0.5 - 0.8 of the absolute melting temperature, with the result that the particles join together spontaneously. The most important driving force for this spontaneous process is the reduction of the solid/vapour surface area as particles fuse together to form necks, and larger particles grow at the expense of the smaller ones. The driving force may be modified somewhat by chemical reactions and phase transformations during the sintering cycle.

The material transport mechanisms for consolidation can involve bulk transport mechanisms such as plastic deformation and grain boundary sliding, and can involve several diffusion processes such as volume diffusion, grain boundary diffusion, surface diffusion, and gas phase diffusion. All of these diffusion processes contribute to neck

growth but only certain ones contribute to densification. Material transport by low activation energy mechanisms, such as surface diffusion or gas phase diffusion, result in considerable neck growth, but pores shrink only when volume diffusion and grain boundary diffusion are active (see Aller [11]).

In solids with a high degree of covalent bonding, such as Si_3N_4 and SiC, the self-diffusivity is poor and therefore volume and grain boundary diffusion is slow. As a result, sintering of these compounds is difficult. At low temperatures atomic mobility is too low for densification, and at temperatures high enough for appreciable atomic mobility these compounds tend to dissociate rather than consolidate.

2.2.1 Si_3N_4

In the case of Si_3N_4, one way to promote sintering is to form a liquid phase at a temperature below that at which significant decomposition of Si_3N_4 occurs (i.e. about 1820°C in air). The liquid phase can be achieved by mixing into the starting powder small amounts of additives such as MgO, Al_2O_3, and Y_2O_3 which react with SiO_2 on the Si_3N_4 particle surface to form an oxynitride liquid at temperatures as low as 1600°C. Provided that the composition and viscosity are suitable, this liquid phase allows transport and rearrangement of the starting material at a greatly accelerated rate by a mechanism in which the starting Si_3N_4 particles dissolve into the liquid and the phase of Si_3N_4 is precipitated out as elongated interlocking grains. Upon cooling, however, the liquid phase solidifies into a grain boundary phase that can become fluid or even become unstable at temperatures greater than about 1000°C, thereby seriously degrading both the refractory and mechanical properties of the Si_3N_4 material.

Numerous approaches have evolved to minimize the effects of the grain boundary phase. One way is to carry out sintering in an atmosphere that has been modified to increase the partial pressure of N_2. In this way volatilization of Si_3N_4 is suppressed, densification can be achieved with less additive, and less grain boundary phase is formed. Another method involves the addition of nucleating agents such as TiO_2 and ZrO_2 to promote crystallization of glassy intergranular phase. The resulting grain boundary crystalline phase can lead to improved refractory properties in the final material, (see Braue et al.[12]). A third method involves mixing in additives which promote sintering, but

which result in a single phase solid solution being formed rather than two solid phases. Tabata et al.[13] have found that this result can be achieved through additions of $BeAl_2O_4$.

The difficulties associated with sintering Si_3N_4 has also led to the development of a completely new class of ceramic materials called 'sialons' - an acronym given to phases in the Si-Al-O-N and related systems. In these materials Si_3N_4 powder is mixed with an equimolar mixture of Al_2O_3 and AlN with the consequence that the Si_3N_4 crystal structure is maintained, but at some lattice positions Al substitutes for Si, and O substitutes for N. The result is a solid solution 'alloy' of Si_3N_4 that is thermodynamically more stable than Si_3N_4 at high temperature. With most sialons a liquid phase is still required to assist sintering, but the addition of Y_2O_3 can lead to a crystalline grain boundary phase (e.g. yttrium-aluminum-garnet or 'YAG') which is stable up to about 1300°C (see Jack[14]).

2.2.2 SiC

The sintering of SiC also requires addition of sintering aids to the starting powder to promote a desired chemical reaction or the formation of a liquid phase. The usual aids are B, C, or Al. The effects of these additions are not well understood (see Hannink et al.[15]) although there are indications that modifications to free surface/grain boundary chemistry are important. This seems to be the case for B, which is known to dissolve into the SiC particles, and B dissolution may somehow increase the diffusivity of the Si and C atoms. The addition of C is thought to aid sintering by reacting with SiO_2 on the surface of SiC particles to form new SiC and CO gas, and also by suppressing the volatilization of SiC into free Si. Note also that there is an interactive effect between B and C insofar as CO, produced by C reacting with adherent SiO_2, can in turn react with B to produce BO, which removes the B from any further role in the sintering[9].

Fully dense SiC that has been sintered with Al additions exhibits an intergranular glassy phase (see Moussa et al.[16]) and this might suggest that Al aids the sintering process by forming a liquid phase.

2.3 Pressure Assisted Sintering

Ceramics can also be fabricated by application of pressure at high temperature, which often combines the forming and sintering into a single step. This can eliminate the need to deal with a green compact. More importantly, however, the simultaneous application of pressure and heat can result in material with higher final densities and finer grain sizes. The improvement is due to an increased driving force for sintering through a combination of sintering mechanisms involving plastic flow (due to stresses set up at points of particle contact) and sintering mechanisms involving diffusion.

Hot pressing shares many similarities with cold pressing - e.g., ceramic particulate is filled into a die and uniaxially pressed - except, of course, that in this case pressing is carried out at elevated temperature. Typical pressures can be up to 400 MPa, and temperatures are typically about 1700°C for Si_3N_4 and about 2000°C for SiC. Graphite is the most widely used die material and this often necessitates that the operation be carried out in a non-oxidizing atmosphere. At these high temperatures the die material can also react with the ceramic itself, and a reaction inhibitor, such as boron nitride (BN) is used to coat the die. As is the case with cold pressing, this fabrication technique is limited to providing relatively simple shapes.

In recent years 'high pressure hot pressing' has emerged as a possible means to consolidate particulate without the use of sintering aids, although this technique would appear to be limited to fabricating components of small dimensions. High pressure has been achieved using apparatus similar to that used for diamond synthesis (up to 5.5 GPa[17]), and using shock loading generated by a momentum trap method (up to 77 GPa[18]).

The usual way of 'hot isostatic pressing' ceramics involves first encapsulating the material under vacuum, and then subjecting it to an isostatic gaseous pressure (up to 200 MPa) at high temperature (up to 2000°C) in a specially designed autoclave. The encapsulation material must be non-reactive at high temperature, yet be able to flow and transmit the gas pressure uniformly to the ceramic body. Various high temperature glasses (e.g. fused silica, Vycor) and refractory metals (e.g. Mo, Ta) are commonly used as encapsulation materials. Fig. 2 illustrates a capsule being HIP'ed. HIP'ing has the potential to produce high density ceramic components of complex shape and there are

studies which suggest that this can be achieved without using sintering additives. These studies and others dealing with HIP processing of ceramics are discussed in Section 3.

2.4 In-situ Chemical Reactions

In the case of ceramic components formed by sintering the matrix chemical composition of the final product is the same as the starting particulate. That is, sintering serves only to consolidate the particulate material into a compact. There are, however, other fabrication processes by which the final product is achieved through a chemical reaction, in which case the final composition may differ substantially from that of the starting material.

Reaction bonding is a process that is used particularly with Si_3N_4 and SiC, and involves the reaction of Si metal with a nitriding or carbiding agent to produce the ceramic (see Davidge [7]). Bonding occurs simultaneously with the reaction as the reaction front progresses. For example, to produce reaction bonded Si_3N_4, a green body of Si metal powder is first prepared by a suitable technique such as pressing, extruding, rolling, or flame spraying. After burning out any binder material, the green body is fired in a nitrogen atmosphere at temperatures initially just below the melting point of Si (1410°C) and then, once a skeleton of Si_3N_4 is formed the temperature is raised above the Si melting point. The total firing time can be over a period of days. The resulting Si_3N_4 is very pure but since porosity is essential to allow access of the nitrogen, it is difficult to produce a final material containing less than about 10% porosity.

SiC can be made by a similar technique in which a mixture of very fine C and SiC is reacted with molten Si. However, the final microstructure typically contains about 10% residual free Si, rather than residual porosity, and the presence of this comparatively low melting point intergranular phase seriously limits the high temperature capability of reaction bonded SiC.

'Chemical vapour deposition' is a process which was originally developed as a means of coating a substrate by an elevated temperature gas phase reaction. For producing SiC, the most common method involves thermal decomposition of methyl trichlorosilane (CH_3SiCl_3) to SiC at a temperature of about 1000°C, and SiC vapour deposits as a solid

onto the substrate. This principle has successfully been applied to building up of a matrix material through 'chemical vapour infiltration' of a porous preform, with the result that a composite material is produced (see Caputo et al.[19]). Appropriate manipulation of temperature and pressure gradients is the key to attaining a product of reasonable density within a reasonable time period, but, similar to the case of reaction bonding of Si_3N_4, retained porosity of the order of 6 to 8% is inevitable.

2.5 Discussion

Numerous problems can arise when using a forming plus sintering route in attempting to produce advanced structural ceramic of high quality. To start with, a binder material is required in many forming operations, but binder residue leftover from burning out can have deleterious effects on the final properties of supposedly 'high purity' sintered ceramic. It is desirable, therefore, to use as little binder as possible, or to use a binder material that can be removed completely prior to sintering. With regards to this last point, efforts have been made to use frozen water as a binder material (see Okunda[20]).

Another problem associated with binder burnout, and with the drying stage in methods like sol-gel processing or slip casting, is pronounced shrinkage of the compact. Cracking may result if the operation is not carefully controlled.

Problems also arise during the sintering stage, especially in the case of Si_3N_4 based or SiC based ceramic. Sintering additives are necessary to aid densification and consolidation of these materials but these additives can form an intergranular glassy phase which degrades the high temperature properties of the ceramic. Some efforts have been made to crystallize this intergranular phase by means of appropriate thermal treatments and/or nucleating agents (see Section 2.2.1), but even crystalline intergranular phases will be less desirable than the main Si_3N_4 or SiC phase.

In a comprehensive overview of Si_3N_4 based ceramics, Ziegler et al.[10] remark that by careful choice of starting materials it may be possible to assist sintering by producing a liquid phase that becomes absorbed into solid solution as sintering progresses. In this way no liquid phase would be present upon cooling to result in the undesired intergranular

glassy phase. However, such a feat requires very strict control over surface chemistry as well as the bulk chemistry of the particulate starting material, and Ziegler et al. note that most attempts have not been completely successful. The results of Tabata et al.[13], using $BeAl_2O_4$ additions, perhaps offer some hope.

3. HIP'ing of Si_3N_4 and SiC

HIP'ing appears to be an attractive alternate route to producing high quality structural ceramics. The method can be used to produce components of complex shape, and has been shown to be successful at closing up residual porosity in many materials. In addition, the application of pressure simultaneously with heat increases the driving force for sintering, and it may be possible to reduce, or even eliminate, the necessity for sintering additives. This improvement in microstructure due to reduced porosity and less intergranular glassy phase, combined with the incorporation of SiC whisker reinforcement may result in a ceramic of sufficiently high quality to be considered for use in gas turbine aero engines.

This part of the presentation surveys the previous work that has been carried out to produce ceramic based on Si_3N_4 or SiC. Much of this survey is based on a synopsis prepared by Davidge et al.[21]

Section 3.1 gives a brief introduction to the various routes which have been followed to produce ceramic by HIP'ing. Sections 3.2 and 3.3 follow with reviews of individual studies that have been carried out on Si_3N_4 and SiC based material and Tables 2 and 3 list results of some mechanical testing.

3.1 HIP'ing Routes

There are many ways in which HIP'ing can be used to produce ceramic, and these are summarized in Fig. 3.

As mentioned in Section 2.3, the usual way to process ceramic by HIP'ing is to first encapsulate a green compact under vacuum, and have the gas pressure act on the capsule. In this way, components with open porosity can be HIP'ed to full density. Interestingly enough, it does not appear that direct densification of ceramic particulate in a near-net-shape capsule has been reported in the literature.

Encapsulation methods can be grouped roughly into three categories and each are discussed below. It is worth noting that encapsulation technology is an important commercial factor in a highly competitive market, often involving long periods of development by trial and error, and as a result, specific details are often confidential.

Components of simple shapes, such as cylinders, can be encapsulated in glass tubes or in welded metal sheet containers. Shapes of greater complexity can be HIP'ed this way if components are placed in an inert powder (e.g. BN) which acts as a medium to transmit pressure. For components of still greater intricacy, complex metal or glass capsules can be made but the cost becomes very high.

A second encapsulation method involves coating the component with one or more layers of glass particles. The component is sealed off by heating under vacuum until the glass layer softens. This is known as the 'glass particle' method. A variant known as the 'glass bath' method involves packing the component into a glass powder bed and heating under vacuum until the glass liquifies and seals the component.

The third encapsulation method, the so-called 'sinter canning' technique, involves coating the component with a highly sinterable powder mixture, and then sintering under vacuum to form a gas tight skin. Using a powder for the coating of similar composition to that of the component results in a very good thermal expansion match.

An alternative HIP route that has been applied to ceramics is simply to HIP components that have already been produced by some forming and sintering operation. (Note: past studies often refer to HIP'ing after sintering by the somewhat misleading term of 'post HIP'ing'). In this case, HIP'ing is carried out to close up residual porosity and heal internal cracks. However, this method is effective only if the porosity is not surface connected, and even if this is the case, pores containing gas will only be reduced in size and not eliminated completely.

A third route is to 'sinter HIP', i.e. place a green compact in the HIP vessel, sinter to a state of closed porosity, and without cooling, HIP to final density. This has the economic benefit of eliminating one complete heat/cool cycle in the processing, and can be important in situations where cooling induces irreversible microstructure changes

which negatively affect densification. If the sintering stage is carried out under vacuum, the porosity remaining after sintering will contain little gas, and a higher density will be attained after the HIP'ing stage.

3.2 Silicon Nitride

3.2.1 HIP'ing of Encapsulated Powder

Larker et al.[22] were the first to report the successful application of HIP'ing to consolidate Si_3N_4 powders: one being a high purity powder containing some amount of Y_2O_3 as a sintering aid, and the other being a comparatively low purity powder containing nothing that was added intentionally. In both cases, the powders were milled to a fine particle size before cold isostatic pressing at 600 MPa into green compacts. The compacts were placed into a capsule of silica or borosilicate glass, and the capsules were then evacuated at elevated temperature and sealed. It is interesting to note that the authors did not use anything as a reaction barrier between the compact and the glass, and even commented that there was no evidence of any reaction having taken place during the operation.

HIP'ing was carried out in two steps. In the first stage the temperature was increased to the softening point of the glass, and some pressure applied, so that the glass conformed to the shape of the compact. The temperature was then increased to 1700 to 1800°C and the pressure was increased to over 100 MPa. These final conditions were held for at least one hour. Larker et al. claimed that Si_3N_4 ceramic of 'full' density was produced. Three point bend strength tests were carried out, and the Si_3N_4 with Y_2O_3 as an additive exhibited a mean strength of 554 MPa when tested at 1370°C. The low purity Si_3N_4 had a bend strength of 346 MPa at 1370°C, and of 655 MPa at room temperature. The result for the HIP'ed sample containing Y_2O_3 is compared with typical results for hot pressed Si_3N_4 and reaction bonded Si_3N_4 in Table 2, and it may be seen that there is a modest improvement in high temperature bend strength. (Note: for ceramic materials the bend strength is often called the 'modulus of rupture' and written as MOR).

Yeh and Sikora[23] carried out an investigation on Si_3N_4 powder of a similar quality as the low purity powder investigated by Larker et al. No sintering aids were added, and

no milling was carried out prior to cold isostatically pressing the powder to 430 MPa. The compacts were placed in quartz or Mo capsules, evacuated, and then sealed. No mention is made of a reaction barrier in the capsule. Yeh and Sikora used both a conventional gas pressure HIP and a hydraulic pressure HIP to carry out the investigation, but there were various problems with the apparatus, and no systematic study of the relationship between temperature, pressure, and time was possible. Nonetheless, the authors found that material HIP'ed for 1 hour at 275 MPa and 1760°C achieved up to 95% of the theoretical density (T.D.), while material HIP'ed for 2 hours at 310 MPa and 1260°C achieved up to 94% T.D. A TEM study suggested that recystallization of the material had occurred, and it was proposed that powder impurities may have contributed to densification, but there was no mention of intergranular glassy phases being detected in the TEM. No mechanical testing was carried out.

Wills et al.[24] HIP'ed high purity Si_3N_4 powder mixed with 1 to 5 wt% Y_2O_3. The mix was milled with Si_3N_4 balls before being cold isostatically pressed to 200 MPa and encapsulated in Ta. The compacts were HIP'ed for 1 hour at 200 MPa and 1725°C. The authors found that 5% Y_2O_3 was required at these HIP conditions to achieve a high density (>99% T.D.) Compressive creep tests were carried out in air at 1350°C and 1500°C. The results were compared with results obtained from commercially available hot pressed Si_3N_4 and judged to be superior. The authors also mention that four point bend strength tests were carried out, but, interestingly enough, the results are not reported.

In a set of two publications, Yeheskel et al.[25,26] report the findings of their study of a high purity Si_3N_4 powder, mixed with 0 to 10 wt% Y_2O_3 sintering additive, that was HIP'ed at 90 MPa and 172 MPa, and at temperatures ranging from 1500 to 1800°C, for 110 minutes. The powders were blended, rather than milled, to avoid the risk of contamination from milling media. The powders were cold isostatically pressed to 200 MPa prior to being encapsulated in Ta canisters, and then out gassed at 550°C or 950°C under vacuum before being sealed by electron beam welding. The authors found that the density of the final material increased systematically with increasing addition of Y_2O_3, with increasing temperature, and with increasing pressure. The density of the sample containing 0% Y_2O_3, and pressed at 172 MPa and 1800°C, was 84% T.D. The density of the sample containing 10% Y_2O_3, and pressed under the same conditions, was 97% T.D. A

TEM study showed regions of a glassy phase in between Si_3N_4 grains. Elastic moduli were measured by a pulse-echo overlap technique, and were found to increase systematically with density.

Koizumi and co-workers[27] investigated HIP'ing of eight high purity Si_3N_4 powders over a range of temperatures, pressures, and times. No sintering aids were intentionally added, but the powder was milled with Al_2O_3 balls prior to cold pressing (to 150 MPa), and the authors observed a 0.3 wt% increase in the powder after milling. The compacts were 'calcined' for a few minutes at 1400°C under vacuum, placed in a BN capsule, and in turn placed in a high silica glass capsule that was subsequently evacuated and sealed. This capsule was then placed into another capsule, made of borosilicate glass, which was also evacuated and sealed. The capsules were placed in the HIP, heated to the softening temperature of the glass under 2 MPa of pressure, and the temperature and pressure were then simultaneously raised to the desired conditions. The final temperature ranged from 1300 to 1900°C, the final pressure was either 100 MPa or 200 MPa, and the hold time varied up to 90 minutes. The authors found that maximum density was attained after HIP'ing in the range from 1650 to 1750°C, with higher temperatures resulting in decreased density due to decomposition of Si_3N_4. Density was found to increase with increasing pressure, with the highest density at 100 MPa pressure being only 77% T.D., while the highest density attained at 200 MPa pressure was 94% T.D. For samples HIP'ed at 1700°C and 200MPa, densification proceeded rapidly within 30 minutes, and thereafter levelled off. The Vickers microhardness of these samples measured at room temperature ranged as high as 1000.

These results for Si_3N_4 powders containing no intentional sintering additive were compared with results obtained from the same powders containing one of various sintering additives (3.2% YN, 4.0% AlN, 4% Mg_3N_2, up to 3.2% Y_2O_3). All of the samples containing additive attained >97% T.D. and exhibited room temperature Vickers microhardness values near 2000.

In a later presentation, Koizumi and co-workers[28] further investigated the potential of non-oxide sintering aids, in the hope that these additives would not form a glassy phase between Si_3N_4 grains. The additives investigated were: YN, AlN, Mg_3N_2, TiN, ZrN, VN, NbN, TaN, and HfN. However, each of these additives was milled together with the Si_3N_4

using Al_2O_3 balls, and there may have been Al_2O_3 contamination. The powders were cold pressed, and the compacts were pre-fired for 1 hour at 1200°C under vacuum. The samples were HIP'ed at 150 MPa and 1650 to 1800°C for 1 hour, and it was found that while the sample containing 5% AlN attained a density of 96% of theoretical, samples which contained 5% YN or 5% Mg_3N_2 reached 100% T.D. Microhardness of the samples was measured at temperatures up to 1200°C under vacuum, and was found to decrease steadily with increasing temperature. It was argued that if oxide sintering aids had been used instead, the microhardness decrease would have been more dramatic.

Koizumi and co-workers[29] reported the results of another investigation, this time on four high purity Si_3N_4 powders without sintering additives. No mention was made as to whether or not the powders were milled. The powders were cold isostatically pressed into pellets at 100 MPa, and pre-fired for 1 hour at 1200°C under vacuum before being placed in BN, folded in Ta foil, and encapsulated in a Pyrex glass container. The sealed sample was heated to 750°C under 2 MPa gaseous pressure to allow the glass to soften, and the temperature and pressure were raised to 1850°C and 180 MPa, respectively, for 1 hour. The final densities achieved ranged from 97.8 to 99.3% T.D. and room temperature Vickers microhardness values were near 2600. Microhardness measured up to 1200°C under vacuum remained near 1000. Three point bend strength measured at room temperature was up to 836 MPa. However, room temperature K_{IC} measured by an indentation method was found to be only about 3.5 MPa $\sqrt{m}$, which is considerably less than typical values for hot pressed Si_3N_4 that contains sintering additives (see Table 2). After observing the fracture surfaces under a scanning electron microscope, the authors attributed the low toughness value to the lack of an energy absorbing intergranular glassy phase, and to the microstructure consisting of equiaxed grains, rather than of elongated interlocking grains typical of Si_3N_4 that has been densified using additives.

Okada et al.[30] reported results of a study carried out on four high purity Si_3N_4 powders which were mixed with: no additives, 0.5 to 5.0 wt% Y_2O_3, and a Y_2O_3 + Al_2O_3 mixture typically used in uniaxial hot pressing. The powders were cold isostatically pressed prior to being placed in a BN capsule which was subsequently vacuum sealed using a glass powder pressing technique. The samples containing no additive were HIP'ed for 2 hours at 150 MPa and at 1800, 1900, or 2000°C. Only one of the samples HIP'ed at 1900°C attained >99% T.D., but all samples HIP'ed at 2000°C did. Bend strength at room

temperature of the samples HIP'ed at 2000°C ranged as high as 650 MPa, while bend strength at 1400°C ranged even higher; to as much as 750 MPa. A TEM study revealed only a very small amount of intergranular glassy phase. The samples containing Y_2O_3 were HIP'ed for 2 hours at 150 MPa and 1750°C, and when the addition was >1% Y_2O_3 the density attained was >99.5% T.D. Both bend strength at room temperature and bend strength at 1200°C increased with increasing Y_2O_3. Bend strength values for samples containing 5% Y_2O_3 were 850 MPa at room temperature, and 500 MPa at 1200°C. The samples containing Y_2O_3 + Al_2O_3 were HIP'ed for 2 hours at 150 MPa and 1700°C, and the samples attained near 100% of theoretical density. The bend strength at room temperature was 950 MPa, while the bend strength remained as high as 755 MPa at temperatures up to 1200°C. However, note that this value for high temperature strength was maintained to 1400°C for the same material HIP'ed with no additives.

Pejryd[31] HIP'ed high purity Si_3N_4 containing from 0 to 6 wt% of an equimolar mix of CaO and MgO as sintering aid. The powders were milled using Si_3N_4 balls and encapsulated according to a technique similar to that described by Larker[22]. It is not clear whether the powders were compacted prior to encapsulation. The HIP'ing was carried out for 1.5 hours at 160 MPa pressure and at temperatures from 1550 to 1750°C. The samples containing no additive and HIP'ed at 1750°C attained up to 95% T.D., while all samples containing additive reached full density at all temperatures. Vickers hardness was measured up to 1000°C in air, and was found to decrease dramatically with increasing temperature. In a comparison of hardness values measured at room temperature it was found that hardness decreased with increasing additive concentration, and decreased with increasing HIP'ing temperature. Room temperature fracture toughness was measured by an indentation method, and was found to increase with increasing additive concentration, and with increasing HIP temperature to a value of 8.5 MPa $\sqrt{m}$ for a sample HIP'ed at 1750°C and containing 6% additive.

3.2.2 Post HIP'ing of Reaction Bonded, Sintered, or Hot Pressed Si_3N_4

In a series of three presentations Heinrich, Bohmer and co-workers[32,33,34] have reported the results of post HIP'ed reaction bonded Si_3N_4 containing from 0 to 7.0 wt% Y_2O_3 or 0 to 5.0 wt% MgO as sintering aid. The samples were encapsulated in fused silica, evacuated, sealed, and then placed in the HIP vessel. The temperature was raised

to the glass softening point, and then temperature and pressure were raised simultaneously to the maximum and held for up to 2 hours. The temperature was 1750°C for all cases and the pressure was varied from 50 to 200 MPa. All samples containing sintering aid achieved full density at pressures >50 MPa while samples containing no sintering additive exhibited a maximum of 98% T.D. at 200 MPa HIP pressure. These densities compare with about 78% T.D. for the starting reaction bonded material. The authors found that room temperature bend strength increased with increasing additive, up to a maximum of 800 MPa for samples containing 7.0% Y_2O_3.

The authors have also HIP'ed sintered Si_3N_4, both with and without encapsulation[35]. Samples containing 0 to 7% Y_2O_3 were HIP'ed with encapsulation at 200 MPa and 1750°C for 2 hours. However, in the case of post HIP'ing without encapsulation the authors found that it was necessary to add Al_2O_3 to allow sintering to a closed-pore state prior to HIP'ing. In all cases room temperature bend strength, bend creep resistance at 1350°C in air, and oxidation resistance at 1350°C in air, were inferior to that exhibited by the post HIP'ed reaction bonded Si_3N_4.

Richerson and Wimmer[36] also post HIP'ed reaction bonded Si_3N_4 containing from 0 to 7.0 wt% Y_2O_3. They encapsulated their samples in evacuated tubes of Ta sheet or fused silica glass, with BN powder used as a reaction barrier. The HIP'ing was carried out at 207 MPa and 1750°C for 1 hour. Densification did not occur in the sample containing no additive, but samples containing >3% Y_2O_3 densified to >95% T.D. Elevated temperature bend strengths ranged up to 628 MPa at 1375°C for material containing 5% Y_2O_3. The authors also carried out stress rupture tests in bending and found that one sample survived for 117 hours at 1400°C under a peak bend stress of 345 MPa.

Hirota et al.[37] post HIP'ed sintered Si_3N_4 samples, containing 2.2 wt% Al_2O_3 + 1.3 wt% MgO + 2 wt% SiO_2, without employing encapsulation. The pressing was carried out under 126 MPa of N_2 gas pressure at temperatures ranging from 1500 to 1750°C and for periods of up to 14 hours. The density increased from 98% T.D. to nearly 100% T.D. after 6 hours. The authors suggested that some of the densification was due to nitridation of SiO_2 to Si_3N_4. The room temperature bend strength improved from about 500 MPa for the starting material to about 700 MPa after HIP'ing at 1750°C.

Fujikawa et al.[38] post HIP'ed non-encapsulated samples which had been hot pressed, and which contained either 5 wt% MgO or 6 wt% Y_2O_3 as sintering additives. The pressing was carried out both under Ar and under N_2 gas pressures, but neither the pressures nor the temperatures are given by the authors. The densities increased both in Ar and in N_2 atmospheres as a result of the HIP treatment, but the treatment in N_2 resulted in the greater increase in density. The room temperature bend strength of the N_2 HIP'ed samples ranged as high as 740 MPa.

In a series of three presentations, Wotting and Ziegler[39,40,41] reported various findings from a multi-faceted study involving the post HIP'ing of Si_3N_4 without encapsulation. They looked at sintered Si_3N_4 and at hot pressed Si_3N_4 containing various additions of Y_2O_3, Al_2O_3, MgO, and SiO_2 as sintering aids, under a wide range of HIP conditions. HIP temperatures were between 1750 to 1980°C, pressures between 180 to 200 MPa, and the pressurizing gas was either N_2 or Ar. Time was varied from 10 to 120 minutes. The results are not very clearly presented, but it can be gathered that post HIP'ing of sintered Si_3N_4 resulted in significant increases in density to a maximum of 96% T.D., an increase in the room temperature bend strength to a maximum of 720 MPa, and a moderate increase in room temperature fracture toughness to a maximum of 8 MPa $\sqrt{m}$. On the other hand, post HIP'ing of hot pressed Si_3N_4 generally resulted in little if any increase in density, a moderate decrease in bend strength, and a moderate decrease in fracture toughness.

3.2.3 Sinter HIP'ing

Iturriza et al.[42] have studied densification of Si_3N_4 by a route that can be viewed as true sinter HIP'ing. They looked at Si_3N_4 powder mixes containing 3 wt% Y_2O_3 plus 0 to 3 wt% Al_2O_3, and at mixes containing 6% Y_2O_3 plus 0 to 6% Al_2O_3, which were milled together using Si_3N_4 balls. The powders were compacted by cold pressing to 100 MPa. Sinter HIP'ing was divided into 3 stages. In the first stage, the compacts were sintered under 0.5 MPa N_2 or Ar pressure at a temperature of 1750°C. Then, without cooling, the pressure was increased to between 10 and 100 MPa at various pressurization rates. In the third stage pressure and temperature (from 1750 to 1850°C) were held at the final values. The total time for the cycle was kept constant at 60 minutes, but the time spent at each stage was varied. The authors found that high density was achieved only if a sufficient

time was spent at the first stage to allow sintering to closed porosity, (i.e. porosity not surface connected), and that the final density increased as the rate of pressurization decreased. However, in no case was the final density >98% T.D.

Greskovich[43] has successfully sintered Si_3N_4 green compacts to >99% T.D. by a route that can be viewed as a low pressure sinter HIP. High purity Si_3N_4 powder was mixed with 7 wt% $BeSiN_2$ and milled together in a steel mill prior to cold isostatic pressing at 200 MPa. During the processing the powder was subjected to a controlled oxygenation in order to have a starting material that also contained about 7 wt% SiO_2. The compacts were first sintered to a closed pore state in 2.1 MPa of N_2 pressure at about 2000°C, and final densification was achieved by increasing the pressure to 7.1 MPa. The hold time at maximum pressure and temperature was about 30 minutes.

Other workers have used N_2 overpressure of up to about 5 MPa (i.e. 50 atm) to sinter Si_3N_4 (see Tăni et al.[44]). However, at such comparitively low pressure the process is really more 'gas pressure sintering' rather than hot isostatic pressing and these studies are not treated in the present review.

3.2.4 Si_3N_4 Matrix Composite Containing SiC Whiskers

There are relatively few reports on investigations into Si_3N_4 based SiC whisker reinforced composite material produced by HIP'ing, and all of those have followed the post HIP route.

Lundberg et al.[45] post HIP'ed reaction bonded Si_3N_4 containing 0 to 30 wt% SiC whiskers. The starting material also contained 6 wt% Y_2O_3 + 2 wt% Al_2O_3 as sintering aid. The reaction bonded samples were placed in glass containers, and were heat treated at 700°C under vacuum before being sealed. HIP'ing was carried out under 200 MPa pressure and 1700°C for an unspecified period of time, and 'full' density was achieved for all samples. However, both room temperature bend strength and indentation fracture toughness decreased markedly with increasing whisker content. This was not attributed to problems in the actual processing, but rather to Co/Fe impurities present in the whisker raw material being carried through the processing stages and ending up as metal inclusions in the microstructure that acted as initiation sites for fracture.

Greil et al[46] post-HIP'ed, without encapsulation, sintered mixtures of fine Si_3N_4 and SiC powder, with the SiC volume fraction ranging from 0 to 60%. The starting material also contained 10.5 wt% Al_2O_3 + 4.5 wt% Y_2O_3 as sintering aid. HIP'ing was carried out under 100 MPa N_2 pressure and 2000°C for about 50 minutes. Samples containing up to about 20% SiC achieved a final density of about 98% T.D., while samples containing more SiC exhibited a lower final density. Room temperature bend strength increased with increasing SiC content to a maximum of about 560 MPa for samples containing 40% SiC. Room temperature fracture toughness measured by an indentation method was found to decrease systematically from 4.2 to 3.0 MPa $\sqrt{m}$ as the SiC content was increased.

Kandori et al.[47] post HIP'ed, without encapsulation, sintered Si_3N_4 containing both 0 and 10 vol % SiC whiskers. The starting material also contained 5 wt% Y_2O_3 + 5 wt% $MgAl_2O_4$ as sintering aid. HIP'ing was carried out under 200 MPa of N_2 pressure at temperatures ranging from 1500 to 1900°C for an unspecified period of time. Final densities of the samples containing 10% whiskers were systematically lower than samples containing no whiskers, for all HIP'ing temperatures. However, both room temperature bend strength and fracture toughness of the reinforced material were higher, exhibiting maximums of up to 900 MPa and 9 MPa $\sqrt{m}$ respectively for material that achieved about 98.5% T.D.

3.3 Silicon Carbide

3.3.1 HIP'ing of Encapsulated Powder

Alderborn and co-workers[48,49] HIP'ed four different high purity SiC powders without adding sintering aids. However, some powders were treated by a sedimentation technique in order to remove particles >1 μm in size, prior to being compacted by cold isostatic pressing at pressures up to 300 MPa. The compacts were then heat treated in a reducing atmosphere to lower the oxygen content. The HIP'ing conditions were: 160 to 200 MPa, 1850 to 1900°C, and 1 hour hold time. The authors found that there was a dramatic improvement in the final density for samples in which the large particles were removed. With these samples, 'full' density was achieved, and the room temperature bend strength was as high as 575 MPa for a sample HIP'ed at 160 MPa and 1900°C. This compares well with a typical strength of 500 MPa for commercially available hot pressed SiC (see Table 3).

3.3.2 Post HIP'ing of Sintered or Hot Pressed SiC

Whalen[50] reported the results on post HIP'ing of sintered SiC, both with and without encapsulation. In the case of the former, the encapsulation material was either SiO_2 glass or Ta sheet, but Whalen noted that during HIP processing Ta reacted with SiC to form TaC. It is not stated whether the containers were evacuated prior to sealing. For both encapsulated and non-encapsulated samples the HIP'ing conditions varied between 103 and 207 MPa pressure, 1600 and 2100°C temperature, and hold time of 0.5 to 6 hours. The results are not clearly presented as to whether they apply to SiO_2 encapsulated, Ta encapsulated, or non-encapsulated samples, but it can be gathered that a sample encapsulated in Ta, and HIP'ed for 1 hour at 193 MPa and 1980°C, achieved nearly 100% of theoretical density. It is also apparent that some samples exhibited room temperature bend strengths near 500 MPa.

Watson et al.[51] post HIP'ed, without encapsulation, commercially available sintered SiC for 2 hours, under 138 MPa of Ar pressure, at temperatures from 1850 to 2200°C. HIP'ing resulted in an increase in density for all cases and, in general, an increase in room temperature bend strength to a maximum of 565 MPa. Bend strength at 1200°C was also measured and was found to range up to 579 MPa for material HIP'ed at 2200°C.

Hunold[52] post HIP'ed, without encapsulation, SiC which was sintered with various combinations of 1 wt% C, 0.6 to 1.0 wt% B, 0.6 to 1 wt% Al and 1 wt% AlN as sintering aids. The HIP conditions were: 200 MPa Ar pressure, 2000°C, and 45 minute hold time. All HIP'ed samples exhibited >99% T.D., and room temperature bend strength of up to 525 MPa was reported for material containing 1% Al.

3.3.3 Sinter HIP'ing

Hunold[52] also investigated densification of SiC by a sinter HIP route. The starting powder contained 1 wt% C and 1 wt% Al which was cold isostatically pressed into compacts. In the first stage of densification the compacts were sintered at 1980°C. The sintering time is not given. Without cooling down, the pressure was then built up to either 100 MPa or 200 MPa of Ar pressure, or to 200 MPa N_2 pressure. When full pressurization was reached the temperature was adjusted to either 1900°C or 2000°C and the process

was held for 45 to 240 minutes. Full density (>99% T.D.) was reached only with the samples that were HIP'ed at 200 MPa and 2000°C. The room temperature bend strength results were very similar to those obtained from samples that had been sintered and then post HIP'ed.

4.0 Discussion and Suggestions for Future Work

It can be seen that numerous routes have been followed to produce Si_3N_4 and SiC ceramics by HIP'ing, but some of these routes do not really take full advantage of the potential of HIP'ing to produce ceramics of superior quality. For example, post HIP'ing material that has already been sintered can reduce the size of undesireable pores, but cannot completely eliminate pores that contain gas trapped during consolidation. At first sight, one solution to the problem would be to carry out the sintering step under vacuum and, indeed, this might be possible with SiC. In the case of Si_3N_4 however, sintering under vacuum is not likely to work because some level of N_2 pressure must always be maintained in order to suppress the decomposition of Si_3N_4. The other problem with post-HIP'ing of sintered material is that in order to have sintered material to start with, addition of sintering aids is necessary, and the high temperature properties of the final product can be affected by the resulting intergranular glassy phase. Interestingly enough, and in spite of these shortcomings, it appears that the majority of efforts to produce Si_3N_4 based composite ceramic by HIP'ing has been via this route.

Post HIP'ing of reaction bonded Si_3N_4 may be a more promising route. This is because the remaining porosity after reaction bonding is surface connected and therefore it is possible to have the pores evacuated by sealing the material under vacuum in a gas tight capsule. The studies reviewed in Section 3.2.2 on monolithic reaction bonded Si_3N_4 HIP'ed in this way suggest that strength and toughness can be improved. However, these studies also suggest that sintering aids are once again required for reaction bonded material to be HIP'ed to higher density. The possibility of following this route to produce composite Si_3N_4 has been investigated by Lundberg et al.[45] but, unfortunately, the expected further improvements in strength and toughness were not observed (see Section 3.2.4). It may turn out that careful control over impurity contamination in the starting powder will result in post HIP'ed reaction bonded Si_3N_4 composite with improved properties.

The issue of whether sintering aids are desirable is not clear, especially in the case of Si_3N_4. On the one hand it seems that densifying by conventional sintering or by pressure assisted sintering (e.g. HIP'ing), and obtaining the elongated interlocking microstructure which is thought to give rise to improved mechanical properties, both require some sort of liquid phase to form at the sintering temperature. These factors have led to incorporating additives into the starting powder to help form this liquid phase. On the other hand, the resulting grain boundary phase can be responsible for the ceramic exhibiting inferior high temperature properties. In reality, the situation is not as straightforward as this because factors such as impurities contained in the starting powder and impurities picked up during processing can result in the formation of, or greatly alter the nature of, a liquid phase. This, in turn, can significantly affect grain growth kinetics, grain morphology, and residual porosity - all of which can affect the final properties as much as the presence of grain boundary phase. Add these considerations to HIP processing variables of temperature, pressure, and time and it is obvious that the interrelations leading to the final product can be very complex. Nonetheless, from the study of Okada et al.[30], it seems that even for Si_3N_4 that has been HIP'ed using a sintering aid and still exhibits high strength at relatively high temperature (i.e. 1200°C), the same Si_3N_4 HIP'ed with no sintering aid maintains this high strength to a temperature that is 200°C higher. This supports the view that maximum high temperature capability is achieved by introducing as little sintering additive as possible.

The encapsulated powder HIP route may hold the most promise for producing ceramic of superior quality. Many workers who have followed this route report obtaining a final product with very low porosity using little or no sintering additives (see Sections 3.2.1 and 3.3.1), and report corresponding improvements in mechanical properties over sintered or hot pressed material (see Tables 2 and 3). Note that in all of these studies the starting powder was compacted prior to encapsulation as opposed to simply filling the capsule with loose powder. It is also worthwhile to note that many of the studies utilizing glass encapsulation mention that the temperature was first raised to the glass softening point before significant pressure was applied. Presumably, these measures were taken to ensure that a gas-tight barrier was maintained as the sample underwent consolidation but the reasons are not actually given in any of the studies.

In any event, it does not appear that the encapsulated powder HIP route has yet been used to produce Si_3N_4 based or SiC based composite ceramic, but indications show promise that composite material produced in this manner will contain a minimum of porosity and grain boundary phase, and may exhibit mechanical properties of sufficient standard to be considered for use in gas turbine engines. Because of this promise, and in light of NAE-SML's experience with HIP'ing, this HIP route would be a good area for further investigation.

The questions of which mechanical properties are most relevant, how to evaluate them, and what standard of performance will be deemed 'sufficient', have not been considered in this report, but the topic will need to be addressed as candidate ceramic material becomes available. At present, nearly all reports on the strength of Si_3N_4 and SiC have been described by bend tests, and both fracture toughness and hardness have been described by indentation tests. These techniques have the benefit of being relatively straightforward means of assessing the relative integrity of ceramic materials. However, before these materials are seriously considered for use in critical structural components, properties such as uniaxial tensile behaviour, fatigue behaviour, and creep behaviour will need to be evaluated under proposed service conditions (i.e. 1400°C). The practical complexities involved in such testing are many, but it might be hoped that NAE-SML's experience in characterizing the high temperature behaviour of metallic aero engine materials can provide a useful starting point. An overview of possible methods for evaluating these properties will be the subject of a future report by the author.

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TABLE 1 - Mechanical and physical properties of high temperature materials

(after Lackey et al.[53])

	Young's modulus E (GPa)	density (g/cm^3)	bend strength (MPa) 20°C	bend strength (MPa) 1200°C	thermal expansion coefficient (10-6K-1)	approximate[(A)] maximum use temperature (°C)
Hot pressed Si_3N_4*	300	3.2	700-1000	600[(B)]	3.0	1400
Hot pressed SiC*	210-480	3.2	230-825	425(C)	4.3-5.6	1600
Hot pressed Al_2O_3	380	4.0	280-1030	200[(D)]	7.2-8.6	1800
Partially stabilized ZrO_2	205	5.7	600-700	-	8.9-10.6	1000
Ni superalloy MAR-M-200	220(E)	8.5[(E)]	-	-	15(E)	1050

* - toughness values for Si_3N_4 and SiC are given in Tables 2 and 3.

(A) - Jeal[1]

(B) - Ziegler et al.[10]

(C) - Watson et al.[51]

(D) - Davidge[54]

(E) - INCO data book[55]

TABLE 2 - Typical Results for Si_3N_4

reference	fabrication route	additions	density (% of theo.)	room temp. bend strength (MPa)	high temp. bend strength (MPa)	room temp. fracture tough. (MPa./m)
Conventional Process						
Ziegler et al.[10]	hot pressed	MgO	96	700[4]	550[4] @ 1300°C	6
Ziegler et al.[10]	sintered	*	96	650[4]	-	6
Ziegler et al[10]	reaction bonded	-	80	320**	320** @ 1400°C	2
HIP						
Larker et al.[22]	encap. powder	Y_2O_3	'full'	-	554[3] @ 1370°C	-
Koizumi & co-workers[29]	encap. powder	none	98.7	836[3]	-	3.5
Okada et al.[30]	encap. powder	Y_2O_3 +Al_2O_3	'full'	950**	755** @ 1200°C	-
Okada et al.[30]	encap. powder	none	>99	650**	750** @ 1400°C	-
Perjyd[31]	encap. powder	3%CaO+3%MgO	'full'	-	-	8.5
Heinrich et al.[33]	post HIP	4%Y_2O_3	98	800[4]	-	-
Richerson & Wimmer[36]	post HIP	5%Y_2O_3	>95	575[4]	628[4] @ 1375°C	-
Wotting & Ziegler[40]	post HIP	15%Y_2O_3 +3.4%Al_2O_3	96	720[4]	-	8
Lundberg et al.[45]	post HIP	6%Y_2O_3 +2%Al_2O_3	'full'	900[4]	-	6
Kandori et al.[47]	post HIP	5%Y_2O_3 +5%$MgAl_2O_4$ +10%SiC whisker	98.5	900[4]	-	9

* - not given
4 - four point bend
3 - three point bend
**- test method not given

TABLE 3 - Typical Results for SiC

reference	fabrication route	sintering aid	density (% of theo.)	room temp. bend strength (MPa)	bend strength (MPa) at 1200°C
Conventional process					
Watson et al.[51]	hot pressed	*	97	500[4]	425[4]
Whalen[50]	sintered	*	98	427[4]	-
HIP					
Alderborn & co-workers[48,49]	encap. powder	none	'full	575[4]	-
Whalen[50]	post HIP	*	99	537[4]	-
Watson et al.[51]	post HIP	*	98.7	565[4]	579[4]
Hunold[52]	post HIP	1%Al	>99	525[4]	-

4 - four point bend
* - not given

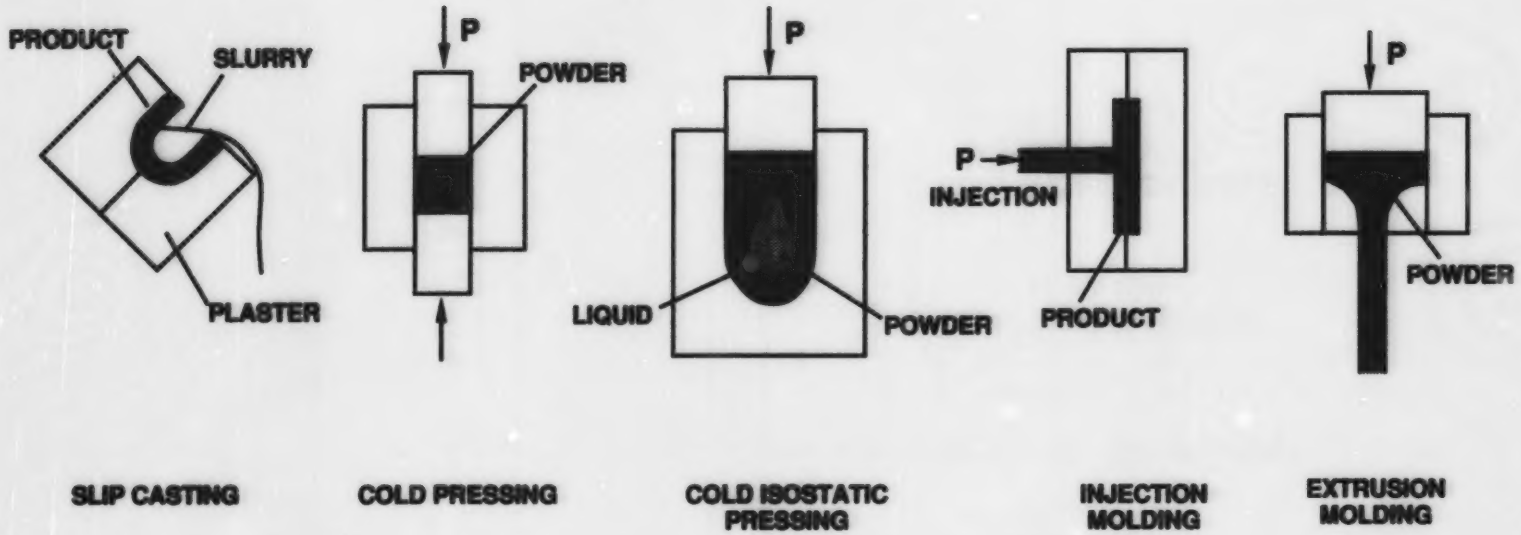

FIG. 1: CERAMIC FORMING METHODS

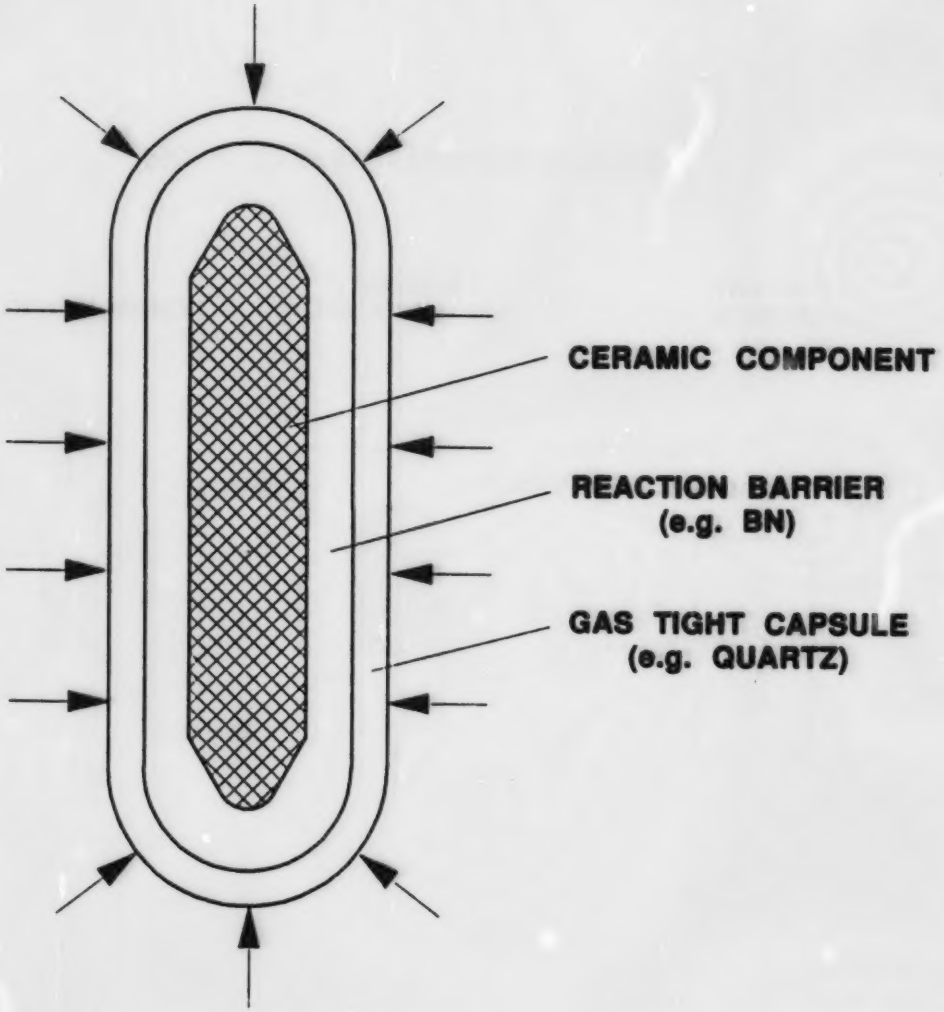

FIG. 2: SCHEMATIC OF ENCAPSULATED CERAMIC BEING HIP'ed

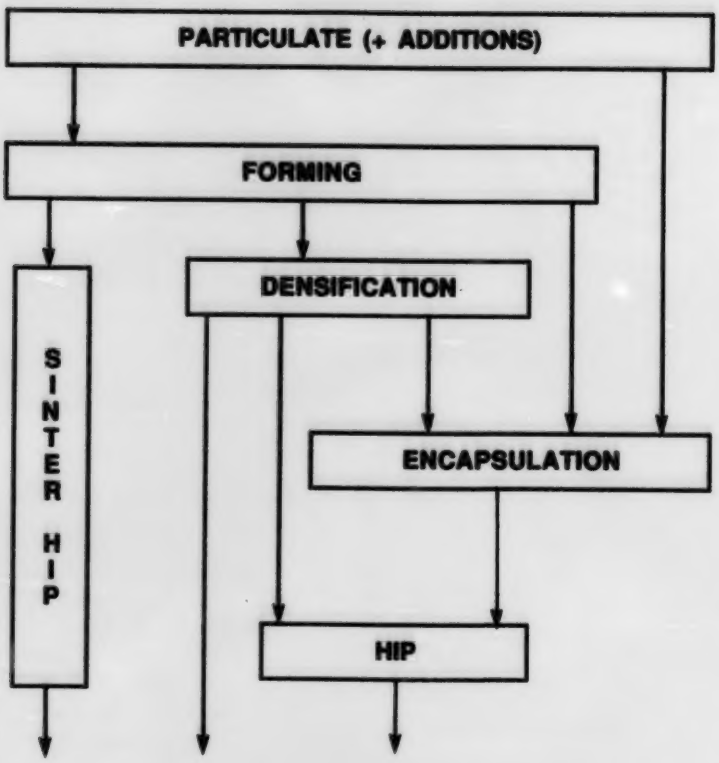

FIG. 3: ROUTES BY WHICH MATERIAL CAN BE PRODUCED BY HIP'ing

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SUMMARY/SOMMAIRE

Si_3N_4 and SiC based advanced ceramics that have been produced by hot isostatic pressing (HIP'ing) have good potential to be used as hot section components in gas turbine aero engines. This report provides background for an NAE-SML investigation of this potential. The report begins with a general overview of the many fabrication methods that have been used to produce both monolithic ceramics and SiC whisker reinforced composite ceramics. This is followed by a comprehensive survey of past efforts to produce Si_3N_4 and SiC based ceramics by HIP'ing. It is apparent that many of these efforts have involved HIP'ing of material that has already been densified by sintering, but such an approach does not really allow the full benefits of HIP processing to be realized. On the other hand, HIP'ing of Si_3N_4 based composite produced by reaction bonding may result in ceramic material of superior quality. It also appears that many previous efforts have resorted to incorporating densifying aids into the starting material, even though high temperature properties may suffer as a result. It is suggested that HIP'ing of vacuum encapsulated Si_3N_4 or SiC particulate which contains SiC whiskers for reinforcement, but which does not contain densifying aids, may be a method of producing ceramic material of sufficient quality to be considered for use in gas turbine engines.

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